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# Nazarov Type Cyclization on an Osmium−Dienylcarbene Complex

Tamara Bolaño, Ricardo Castarlenas, Miguel A. Esteruelas,* and Enrique Oñate

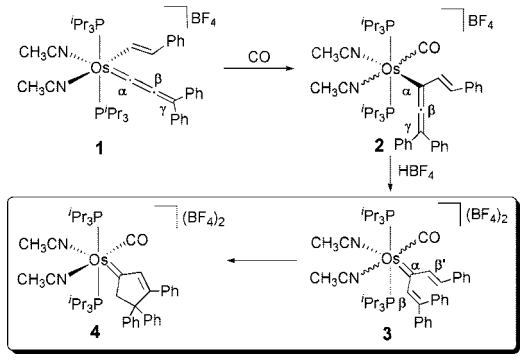
*Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain*

Received November 28, 2008; E-mail: maester@unizar.es

The Nazarov reaction is an acid-catalyzed 4$\pi$-electrocyclic ring closure of dienylketones, which affords cyclopentenones.[1] This type of cyclization has been increasing in interest over the years, due to the importance of the construction of five-membered rings in the synthesis of natural products.[2] However, one potential problem is that the carbonyl group necessary for the cyclization to occur may not be required in the final synthetic target and can sometimes be difficult to remove or modify. One possible solution is to design analogous reactions which do not suffer the carbonyl dependence.

Acyclic dienylcarbene complexes are dienylketone counterparts in which the oxygen atom has been replaced by a transition metal and its associated ligands. Unfortunately, they are very rare.[3,4] However, taking advantage of that for osmium, the equilibrium between species hydride−carbyne and carbene can be shifted toward the oxidized or reduced forms; by means of the control of the electron richness of the metal center with the ligands,[5] we have recently developed a method to prepare acyclic dienylcarbene complexes. It involves the formal insertion of alkynes into the $C_\alpha$−H bond of alkenylcarbene groups.[6] Now, we show that the coordination of an acidic ligand, such as carbon monoxide, to the metal center of these organometallic compounds produces the same effect as the addition of the Lewis acid catalyst to the oxygen atom of a dienylketone, i.e., a Nazarov type cyclization to afford a cyclopentenylidene organic fragment (Scheme 1).

***Scheme 1***




The styryl−allenylidene complex **1** undergoes a rapid intramolecular reduction under a carbon monoxide atmosphere, to give the allenyl derivative **2** as a result of the migration of the styryl group from the metal center to the $C_\alpha$ atom of the allenylidene. The rapidity of the process (faster than 5 min) is consistent with the initial substitution of one of the acetonitrile ligands of **1** by a carbon monoxide molecule, which produces a decrease of the activation barrier for the migration.[5b,7] The recoordination of the substituted acetonitrile to the resulting five-coordinated intermediate affords the allenyl complex, which is isolated at 243 K as a dark red solid in 82% yield. Its $^1$H, $^{13}$C{$^1$H}, and $^{31}$P{$^1$H} NMR spectra reveal that in solution it exists as a mixture of the two possible rotamers resulting from a hindered rotation of the allenyl group around the Os−$C_\alpha$ axis. The hindrance is a consequence of the steric demand of the isopropyl groups of the phosphines and the substituents of the generated organic fragment. The $^{13}$C{$^1$H} NMR spectrum of the new compound shows the characteristic allenyl resonances[5d] at 208.3 and 206.0 ($C_\beta$), 104.5 and 100.7 ($C_\gamma$), and 84.7 and 84.1 ($C_\alpha$) ppm.

Allenyl ligands attached to ruthenium and osmium are nucleophilic at $C_\beta$.[5d,8] In agreement with this, in acetonitrile at 253 K, the $C_\beta$ atom of the allenyl of **2** adds the proton of $HBF_4 \cdot OEt_2$ to give the dienylcarbene derivative **3**, in almost quantitative yield. Complex **3** can be also prepared as a brown solid in 80% yield, by stirring of a dichloromethane solution of [Os{(*E*)-CH═CHPh}-(≡CCH═$CPh_2$)($CH_3CN$)$_2$($P^iPr_3$)$_2$][$BF_4$]$_2$ under a carbon monoxide atmosphere for 10 min. In solution at room temperature, it also exists as a mixture of the two possible rotamers resulting from a hindered rotation of the dienylcarbene around the Os−$C_\alpha$ bond. Thus, two Os$C_\alpha$ resonances at 275.3 and 272.9 ppm are observed in the $^{13}$C{$^1$H} NMR spectrum.

Complex **3** is unstable in solution. In dichloromethane at room temperature, it evolves into the cyclic alkenylcarbene derivative **4** as a result of a Nazarov type cyclization. The $^1$H and $^{13}$C{$^1$H} NMR spectra of this compound, which is isolated as a brown solid in 79% yield, support the formation of the cycle. In the $^1$H NMR spectrum, its resonances appear at 8.60 (CH) and 4.02 ($CH_2$) ppm, whereas in the $^{13}$C{$^1$H} NMR spectrum the Os$C_\alpha$, CH, CPh, $CPh_2$, and $CH_2$ resonances are observed at 287.6, 154.2, 180.4, 68.9, and 80.4 ppm, respectively. In agreement with equivalent phosphines, the $^{31}$P{$^1$H} NMR spectrum contains a singlet at 11.0 ppm. These spectra reveal that from the isomers resulting from the two possible orientations of the five-membered ring, in the perpendicular plane to the P−Os−P direction, only one of them is present in solution. The *Z* disposition of the carbonyl ligand and the CH═CPh bond was inferred from a $^{13}$C,$^1$H-HOESY experiment on the $^{13}$CO-labeled species, which shows the cross-peak between the carbonyl signal and the proton CH resonance of the five-membered ring.

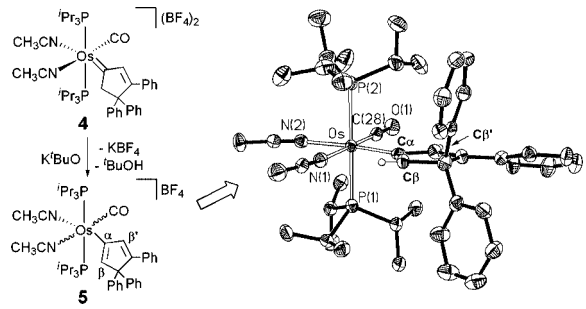
The $CH_2$ group of the cycle is fairly acidic. Treatment of acetonitrile solutions of **4** with 1.2 equiv of K$^t$BuO at 243 K produces its deprotonation to afford the $\eta^1$-cyclopentadienyl derivative **5**, which is isolated as a brown solid in 64% yield. The acidity is enough for decomposing the tetraphenylborate anion into benzene and triphenylborane. Thus, the addition at room temperature of 4.0 equiv of $NaBPh_4$ to dichloromethane solutions of **4** leads to the $BPh_4$ salt of **5**, which has been characterized by X-ray diffraction analysis (Scheme 2).

The structure proves the cyclization of the dienylcarbene ligand of **3**. The coordination geometry around the osmium atom of **5** can be rationalized as a distorted octahedron with *trans* phosphines (P(1)−Os−P(2) = 177.31(5)°) and *cis* acetonitriles (N(1)−Os−N(2) = 83.00(17)°). The Os−$C_\alpha$ distance of 2.086(5) Å is as expected for an Os−C($sp^2$) single bond.[9] In contrast to **4**, but in agreement



10.1021/ja8093058 CCC: $40.75 

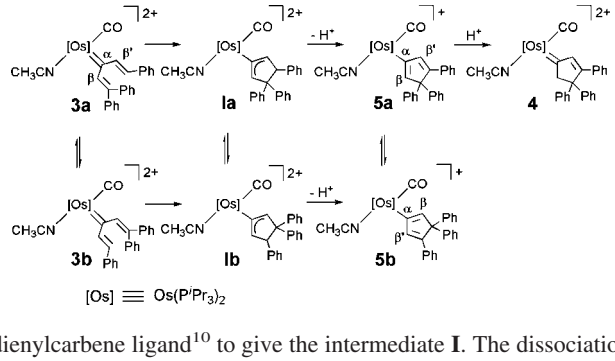
***Scheme 2***




with **2** and **3**, complex **5** exists in solution as a mixture of the two possible rotamers resulting from a hindered rotation of the five-membered ring around the Os−$C_\alpha$ bond. Thus, the $^{13}C\{^1H\}$ NMR spectrum shows two $OsC_\alpha$ resonances at 151.0 and 149.7 ppm.

It has been proposed that the addition of a Lewis acid to the oxygen atom of a dienylketone promotes a thermally allowed $4\pi$ conrotation to afford an oxyallyl cation. This species leads to the cyclopentenone product by a deprotonation−protonation process, via a Lewis acid bound enolate.[1] The formation of **4** can be rationalized in a similar manner, with complex **5** being the organometallic counterpart to the Lewis acid bound enolate (Scheme 3). The carbonyl ligand of **3** promotes the $4\pi$ conrotation of the

***Scheme 3***




dienylcarbene ligand[10] to give the intermediate **I**. The dissociation of $H^+$ from the CHPh group of the formed ring leads to **5**, which adds $H^+$ at $C_\beta$.

The treatment of the rotamers mixture of **5** with $HBF_4 \cdot OEt_2$ produces the instantaneous formation of **4**, which exists as the isomer shown in Scheme 1. In addition, theoretical calculations on octahedral $d^6$ carbene−metal complexes have shown that the presence of a carbonyl ligand *cis* disposed to the carbene imposes a high barrier to the rotation of the carbene around the M−C double bond.[11] Both observations suggest that the protonation of the five-membered ring of **5** takes place by the acetonitrile side; i.e., the carbonyl group appears to exert a protective effect on the $C_\beta$ atom of **5b**. Therefore, the isomerization of **5b** into **5a** is necessary for the full transformation of **5** into **4**. *E*/*Z* isomerization also occurs prior to cyclization for *E* alkyliden $\beta$-ketoesters.[1c]

The formation of **4** from **3** in chloroform-*d* is a first-order process with activation parameters of $\Delta H^\ddagger = 15.7 \pm 0.8$ kcal·mol$^{-1}$ and $\Delta S^\ddagger = -23.8 \pm 1.9$ eu. These results are consistent with the mechanistic proposal depicted in Scheme 3. The negative value of $\Delta S^\ddagger$ suggests that the rate-determining step for the formation of the cycle of **4** is the $4\pi$ conrotation on the dienylcarbene ligand. Furthermore, because in the $^1H$ NMR spectrum the relative intensities between the resonances of the rotamers of **3** are constant during the cyclization, the isomerization processes between rotamers should be faster that the $4\pi$ conrotation.

In conclusion, five-membered rings analogous to those of the cyclopentenones can be constructed from dienylcarbene complexes by a Nazarov type cyclization. Thus, we show that a $\pi$-acceptor ligand, such as carbon monoxide, coordinated to the metal center of an osmium−dienylcarbene complex promotes the $4\pi$ conrotation of the dienylcarbene, to afford a cyclic alkenylcarbene derivative via an $\eta^1$-cyclopentadienyl intermediate. The carbonyl ligand also appears to play a determinant role in the stereochemistry of the final product.

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**Supporting Information Available:** Experimental details for the synthesis, characterization of **2**, **3**, **4**, and **5**, as well as for the crystallographic data of **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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